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EXCITED-STATE ENERGISTICS AND DYNAMICS OF LARGE
MOLECULES COMPLEXES AND CLUSTERS(U) TEL-AVIV UNIV
(ISRAEL) DEPT OF CHEMISTRY J JORTNER ET AL 30 APR 87
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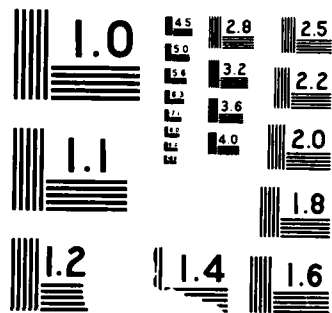
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PROGRESS REPORT FOR THE PERIOD NOVEMBER 1, 1986 - APRIL 30, 1987

5th Periodic Report

1. Title: EXCITED-STATE ENERGETICS AND DYNAMICS OF LARGE MOLECULES, COMPLEXES AND CLUSTERS
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6. PROGRESS IN TECHNICAL APPROACH

New techniques for spectroscopy in supersonic expansions and in the development of specific supersonic sources were developed.

6.A Vacuum Ultraviolet Absorption Spectroscopy in Supersonic Expansions. We have combined the techniques of vacuum ultraviolet (VUV) spectroscopy together with planar supersonic jets, which allows for the interrogation of absorption spectra of large molecules cooled in supersonic expansions in the near VUV region. The experimental setup consists of a high pressure Xe lamp, CaF_2 optics, a vacuum ultraviolet spectrograph and a nozzle slit (0.27x90 mm, repetition rate 9 Hz and gas pulse duration 300 μsec). The characteristics of this spectroscopic setup are: (i) Energy range 6-10 eV. (ii) Spectral resolution 0.1 Å. (iii) Routine measurements of high-energy absorption spectra. (iv) Interrogation of fluorescence excitation spectra of the parent molecule or its photoproducts with limiting quantum yields of $Y \geq 10^{-4}$.

6.B Development of Conical Nozzles for Supersonic Jets. Conical nozzles (nozzle opening angle $\theta = 30^\circ$, and nozzle diameter $D = 0.3$ mm) were constructed and used in conjunction with a magnetic pulsed valve. The use of conical nozzles considerably enhances clustering in supersonic expansions, facilitating studies of large van der Waals complexes and clusters.

7. ACCOMPLISHMENTS OF OBJECTIVES

7.A Energetics of Rydberg States of Jet Cooled Molecules. VUV absorption spectra of benzene, benzene- D_6 and naphthalene cooled in planar supersonic expansions were measured over the range 2000-1600 Å, providing evidence on energetics, line broadening and interference effects.

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- 7.B Rydberg States of Anthracene. Several Rydberg transitions of jet-cooled anthracene were observed in the spectral region 1900-2000 Å. These Rydbergs are superimposed on a broad "background" of $\pi\pi^*$ transitions. Up to now no fluorescence from Rydberg states of polyatomic molecules has been reported. The 1997 Å $n=3$ Rydberg of anthracene reveals fluorescence with a quantum yield of $\sim 5\%$. This fluorescence originates from internal conversion $R \rightsquigarrow S_1$ followed by $S_1 \rightarrow S_0$ emission, as documented by the spectral distribution of the dispersed fluorescence.
- 7.C Intramolecular Relaxation of Rydberg States. Information on intramolecular dynamics of extravalence excitations of benzene was obtained from lineshape analysis. The lineshape of the $^3P_{xy}(0)$ Rydberg is Lorentzian, whose homogeneous width result in the lifetime $\tau = 0.19 \pm 0.02$ psec for C_6H_6 and $\tau = 0.22 \pm 0.02$ psec for C_6D_6 . Semiquantitative information on the lifetimes of some Rydbergs of anthracene was obtained, which fall in the range of ~ 0.1 psec. These lifetime data imply that (i) the relaxation of the Rydberg is characterized by moderate energy gap(s), and (ii) the electronic relaxation rate of the Rydberg is considerably less efficient than that of the intravalence excitation in the same energy domain.
- 7.D Interference Effects between Extravalence and Intravalence Molecular Excitations. We have searched for Rydberg-valence interference effects in large molecules, which are expected to be exhibited in asymmetric Fano-type lineshapes in absorption. For "isolated" Rydbergs, which are superimposed on a $\pi\pi^*$ transition in benzene, naphthalene and anthracene, the absorption lineshapes are symmetric Lorentzians. No line asymmetry and no antiresonances characteristic of Fano profiles were found in that case. The absence of interference effects in this case reveals the manifestation of random interstate coupling of R with the π^* manifold. The random coupling erodes all interference effects. The situation is different for nearly lying Rydbergs, where pronounced R-R-valence interference effects were observed in the absorption spectra of jet-cooled naphthalene in the spectral region 1600-1650 Å, providing information on the homogeneous contribution to high-energy molecular coupling phenomena.

- 7.E Rotational State Dependence of Intramolecular Dynamics. Rotational effects on interstate coupling are of considerable current interest. Absolute fluorescence quantum yields from photo-selected rotational states were measured for the electronic origins of the S_1 state of pyrazine. Strong rotational state dependence was observed providing novel information on interstate coupling for the intermediate level structure. This unique information cannot be extracted from time-resolved decay lifetimes.
- 7.F The Coupling between Intrastate Vibrational Energy Redistribution and Interstate Electronic Relaxation. We have documented some universal characteristics of the decay lifetimes and fluorescence quantum yields from the S_1 manifold of large molecules, which originate from the coupling between intrastate vibrational energy redistribution and interstate electronic relaxation. The time-resolved total fluorescence decay excited by a psec laser from the S_1 state of jet-cooled 9CN-anthracene exhibits nonexponential decay in the energy range $E_v = 1200-1740 \text{ cm}^{-1}$ above the S_1 origin, which does not originate from dephasing but rather manifests the effects of intrastate intermediate level structure for vibrational energy redistribution on intersystem crossing.
- 7.G Coriolis Rotation-Vibration Coupling and Intramolecular Dynamics. We have demonstrated that rotational effects play a central role on intramolecular vibrational energy redistribution in electronic-vibrational excitations of large molecules. Strong rotational effects on the fluorescence quantum yields from vibrational states (above 1000 cm^{-1}) in the S_1 manifold of 9-cyanoanthracene were observed, which demonstrate that Coriolis interactions serve as the dominant coupling leading to intramolecular vibrational energy redistribution (IVR). In contrast to common wisdom, which attributed IVR in large molecules to anharmonic interactions, we have shown that rotational effects play a central role strongly enhancing interstate electronic relaxation.
- 7.H Resonances in Mediated Intersystem Crossing. The mechanisms of direct and of mediated intersystem crossing from the first excited singlet manifold of anthracene and some of its derivatives were explored by the study of the internal and the external heavy atom effect on the fluorescence quantum yields. Pronounced mode selectivity was observed in the vibrational energy dependence of the emission quantum yield in 9-bromoanthracene and 9,10-dibromoanthracene.

7.1 Mediated Intersystem Crossing Phenomenology, Inverse Isotope Effects and Microscopic Level Shifts. We explored the energy dependence of the interstate electronic relaxation rates, k_{nr} , from the S_1 manifold of anthracene and seven of its isotopic and chemical derivatives, which were inferred from quantum yield data. Absolute fluorescence quantum yields, Y , from groups of rotational states within the electronic origin $S_1(0)$ and from vibrational states were obtained over the excess energy $E_V = 0-3000 \text{ cm}^{-1}$ above $S_1(0)$ by the simultaneous interrogation of the fluorescence excitation spectra and of the absorption spectra in seeded, pulsed, planar supersonic jets of Ar. Additional information was obtained from quantum yield data of van der Waals (vdW) complexes of these molecules with Ar. The fluorescence quantum yields from the $S_1(0)$ of anthracene, 9-cyanoanthracene and 9,10-dibromoanthracene were found to be independent of the rotational state, providing further evidence for the rotational independence of k_{nr} from a single doorway state. From the Y data of the electronic origins and from the E_V dependence of Y , we conclude that intersystem crossing (ISC) dynamics of the S_1 manifold is dominated by the interplay between two classes of nonreactive coupling and/or relaxation. (i) Interstate coupling, involving the superposition of direct $S_1 \rightarrow (T_x)$ ISC together with $S_1 - (T_x) \rightarrow (T_1)$ mediated ISC through a sparse or dense (T_x) manifold of a higher triplet state. (ii) Intrastate coupling within the S_1 manifold, which sets in with increasing E_V and which results in intramolecular vibrational energy redistribution (IVR) at high E_V . The dominant role of mediated interstate coupling in ISC dynamics from $S_1(0)$ and from low E_V states was inferred from the inverse deuterium isotope effect on the ISC rates, the extreme sensitivity of k_{nr} of deuterated anthracene to a single H atom substitution, and to level shifts induced by complexing with Ar, as well as from the three orders of magnitude difference between the k_{nr} values from the $S_1(0)$ of 9-bromoanthracene and of 9,10-dibromoanthracene. The onset of the mediated ISC is documented by an abrupt drop of Y in the narrow ($E_V = 617-805 \text{ cm}^{-1}$) energy range for 9,10-dichloroanthracene and by the oscillatory energy dependence of Y versus E_V and the extreme energy sensitivity of Y in the range $E_V = 157-800 \text{ cm}^{-1}$ of 9,10-dibromoanthracene which is attributed to near-degeneracies between S_1 states and the mediating (T_x) states. These resonance effects can be drastically modified by dispersive level shifts induced by complexing with Ar. At high excess vibrational energies some universal features of the E_V dependence of k_{nr} are exhibited. These involve a gradual increase of k_{nr} with increasing E_V at medium energies ($E_V = 1000-1800 \text{ cm}^{-1}$), which correspond to the intermediate level structure for intrastate coupling, and a very weak E_V dependence of k_{nr} at high energies ($E_V = 1800-3000 \text{ cm}^{-1}$), which manifest the effect of statistical intrastate IVR on interstate ISC.

- 7.J Fluorescence Quantum Yields for Highly-Excited States of Large Molecules. Fluorescence quantum yields Y from high electronic excitations of naphthalene, anthracene and tetracene in the energy range 5.0-6.5 eV have been recorded. Y exhibits an exponential dependence on the excess vibrational energy with the slope decreasing with increasing size of the molecule, i.e., the vibrational density of states. These data are characteristic of internal conversion from S_1 to S_0 . These results are of interest regarding recent astrophysical implications of high-energy photophysics of large aromatic hydrocarbons in outer space.
- 7.K Photoisomerization Dynamics of Trans-Stilbene and of Cis-Stilbene. Time-resolved fluorescence lifetimes from photoselected states of trans-stilbene were recorded by the techniques of picosecond spectroscopy in jets using a mode-locked dye laser and a fast photon counting system. Decay lifetimes as short as 100 ± 30 psec were recorded. Extensive information on the energy dependence of the isomerization rates of alkyl stilbenes was obtained, providing information on the role of intramolecular vibrational distribution on the photochemistry in an isolated molecule. The absorption spectrum of jet-cooled cis-stilbene is broad and no vibrational structure could be resolved due to the congestion of broadened low-frequency vibrational excitation. From the low quantum yield $Y \leq 2 \times 10^{-4}$ we infer a S_1 lifetime of $\tau \leq 0.4$ psec, which indicates ultrafast relaxation of this molecule.
- 7.L Photoisomerization Dynamics of Alkyl Substituted Trans-Stilbene. A central issue pertaining to isolated-molecule photochemistry involves the role of intramolecular vibrational relaxation in determining intramolecular dynamics. We have attempted to increase the density of vibrational states by alkyl substitution of trans-stilbene and have explored the isomerization dynamics by picosecond time-resolved spectroscopy. We have obtained the counter-intuitive result that alkyl substitution of trans-stilbene enhances the photoisomerization rates, while general arguments based on the role of IVR and the implications of statistical theories indicate that the rate should be retarded. The results can be accounted for by the modification of the molecular parameters, i.e., threshold energy, by alkyl substitution.

- 7.M Energy-Resolved Photoisomerization Rates. The dynamics of the S_1 and S_2 electronically excited singlet states of diphenylbutadiene was interrogated by fluorescence quantum yield measurements over the very broad energy domain of 0-7500 cm^{-1} above the (false) S_1 origin. The issues of the lack of mode selectivity and the applicability of statistical theories for the description of isolated-molecule photochemistry were explored.
- 7.N van der Waals Complexes of Porphyrins. Excited-state energetics and dynamics of large complexes consisting of porphyrins bound to rare-gas atoms were explored. Detailed spectroscopic information on the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions of the free-base porphine-Ar complex was obtained, providing insight into the structure of this complex as well as resulting in a novel mechanism for microscopic solvent shifts induced by configurational distortions, which are due to complexing.
- 7.O Coupling between Intramolecular and Intermolecular Nuclear Motion in Complexes. Intermolecular vibrations of large van der Waals complexes, which involve the motion of the ligand relative to the large molecule, provide an analogue for surface vibrational motion in a finite system and constitute the precursors of phonon modes in condensed phases. Information on the coupling between intermolecular and intramolecular vibrational motion was obtained for the trans-stilbene-Ar complex.
- 7.P Analogies between Large van der Waals Molecules and Microsurfaces. The binding of rare-gas (R) atoms to large aromatic molecules (M) on the one hand, and to the basal plane of graphite on the other hand, represent two extremes of the interaction of R atoms with ordered arrays of sp^2 hybridized carbon atoms. We have explored the analogies between the characteristics of large van der Waals $\text{M} \cdot \text{R}_n$ complexes and R atoms on graphite surfaces, focusing on structure, packing, orientational registry effects and the nuclear motion of R adsorbates on finite microsurfaces. The elucidation of the structure, energetics and nuclear dynamics of large $\text{M} \cdot \text{R}_n$ complexes rests on semi-empirical model calculations of potential surfaces. These provide a quantitative account of the geometry, the existence of isomers, the dissociation energies and the frequencies of out-of-plane and in-plane vibrational modes for large amplitude intermolecular nuclear motion.

- 7.Q Electron Localization in Clusters. Small clusters exhibit unique physical and chemical phenomena, which are both of fundamental and technological significance, and provide ways and means to explore the "transition" from molecular to condensed-matter systems. We have provided a theoretical study of the structure, energetics and dynamics of an excess electron interacting with an alkali-halide cluster, which was explored by the quantum path integral molecular dynamics method. These studies establish various compositional, structural and size dependence of bulk and surface localization mechanisms of the dynamic process induced by electron attachment.
- 7.R Vibrational Predissociation Induced by Exciton Trapping in Rare-Gas Clusters. The dynamics of exciton trapping, vibrational energy transfer and vibrational predissociation in an electronically excited state of Ar_{13} clusters was explored by classical molecular dynamics. This study constitutes an application of this technique for the dynamics of electronically excited states of large systems. New mechanisms of ultrafast (~ 300 fsec) vibrational energy flow induced by short-range repulsion were documented. In these systems vibrational energy redistribution does not occur and mode selective excitation prevails. In small ($n=13$) clusters the consequences of vibrational energy flow results in reactive vibrational predissociation, leading to the "evaporation" of Ar atoms for the cluster. In larger ($n=55$) clusters a transition from molecular-type reactive behavior to nonreactive vibrational relaxation, which is characteristic of condensed phases, was exhibited.
- 7.S Nonreactive and Reactive Excited-State Dynamics in Mixed Rare-Gas Clusters. We explored the dynamic implications of energy exchange in electronically-vibrationally excited states of mixed rare-gas clusters. The classical molecular dynamics method was applied for the study of vibrational energy flow from electronically excited atomic ($^3\text{P}_1$) states in $\text{Xe}^* \text{Ar}_{12}$ and $\text{Xe}^* \text{Ar}_{54}$, due to short-range repulsive interactions, and the consequences of $\text{Xe}_2^*(^3\Sigma_u^-)$ excimer formation in $\text{Xe}_2^* \text{Ar}_{11}$ and $\text{Xe}_2^* \text{Ar}_{53}$ clusters. We have established the occurrence of an ultrafast vibrational energy flow (~ 300 fsec) from local Rydberg atomic and excimer excitations into the cluster,

7.S (cont'd)

which is accompanied by large configurational dilation around the excited state, due to short-range repulsive interactions. Size effects on cluster dynamics were elucidated, being manifested by vibrational predissociation in small clusters, and by vibrational relaxation and vibrational predissociation in small clusters and by vibrational relaxation and vibrational energy redistribution in large clusters. A gradual transition from reactive molecular type relaxation in small clusters to nonreactive condensed-matter type relaxation in large clusters was documented. Qualitative and quantitative differences between relaxation of excited species initially located in the interior or on the surface of the cluster were established, being exhibited in the details of the vibrational energy flow. In the case of the bulk $\text{Xe}_2\text{Ar}_{53}$, excessive local heating is manifested in cluster melting, which results in mass transport of the excimer to the cluster surface. The many facets of the dynamics of electronically excited mixed rare-gas clusters are amenable to experimental interrogation.

8. PUBLICATIONS

The following manuscripts, supported by this research grant, were prepared and submitted for publication:

- (1) A. Amirav and J. Jortner
Vacuum Ultraviolet Absorption Spectroscopy in Supersonic Expansions
J. Chem. Phys. (Communication) 82, 4378 (1985)
- (2) A. Amirav and J. Jortner
Rotational and Vibrational State Dependence on Intramolecular Coupling and Dynamics in the S_1 State of Pyrazine
J. Chem. Phys. (in press)
- (3) J. Troe, A. Amirav and J. Jortner
Energy-Resolved and Thermalized Photoisomerization Rates of Diphenyl-Butadiene
Chem. Phys. Letters 115, 245 (1985)
- (4) A. Amirav, M. Sonnenschein and J. Jortner
Interstate Coupling and Dynamics of Excited Singlet States of Isolated Diphenylbutadiene
Chem. Phys. 102, 305 (1986)
- (5) U. Even, Z. Berkovitch-Yellin and J. Jortner
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- (6) D. Bahatt, U. Even and J. Jortner
Coupling between Intramolecular and Intermolecular Nuclear Motion in a Large van der Waals Complex
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- (7) Klaus Rademann, Uzi Even, Shlomo Rozen and J. Jortner
Photoisomerization Dynamics of Alkyl Substituted Stilbenes
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Chem. Phys. Lett. 125, 5-11 (1986)

- (8) A. Amirav, J. Jortner, S. Okajima and E. C. Lim
Manifestations of Intramolecular Vibrational Energy
Redistribution on Electronic Relaxation in Large Molecules
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- (9) U. Landman, D. Scharf and J. Jortner
Electron Localization in Alkali-Halide Clusters
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1986, in: Advances in Chemical Reaction Dynamics (D. Reidel
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- (13) Samuel Leutwyler and Joshua Jortner
The Adsorption of Rare-Gas on Microsurfaces of Large
Aromatic Molecules
J. Phys. Chem. (in press)
- (14) Dafna Scharf, Uzi Landman and Joshua Jortner
Atomic and Molecular Quantum Mechanics by the Path
Integral Molecular Dynamics Method
Chem. Phys. Letters 130, 504 (1987)
- (15) A. Amirav and Joshua Jortner
Rotation, Vibration and Electronic Relaxation
Proc. of the CECAM Conference, Orsay, France, 1986
(D. Reidel Publishing Co., Holland, 1986)
- (16) A. Amirav and J. Jortner
Resonances in Mediated Intersystem Crossing of Jet-
Cooled Anthracene Derivatives
Chem. Phys. Letters 132, 335 (1986)
- (17) A. Amirav, J. Jortner, M. Terazima and E.C. Lim
Rotational Effects on Intramolecular Radiationless
Transitions in a Large Molecule
Chem. Phys. Letters 133, 179-184 (1987)
- (18) U. Landman, R.N. Barnett, C.L. Cleveland, D. Scharf
and J. Jortner
Electron Excitation Dynamics, Localization and Solvation
in Small Clusters
J. Phys. Chem. (in press)
- (19) A. Amirav, C. Horwitz and J. Jortner
Optical Selection Studies of Electronic Relaxation from
the S_1 State of Jet-Cooled Anthracene Derivatives
J. Chem. Phys.
- (20) R.D. Levine, S.A. Rice and J. Jortner
Level Structure and Dynamics from Diatomics to Clusters
Advances in Chemical Physics (John Wiley & Sons, New York,
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- (13) Samuel Leutwyler and Joshua Jortner
The Adsorption of Rare-Gas on Microsurfaces of Large
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- (20) R.D. Levine, S.A. Rice and J. Jortner
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Advances in Chemical Physics (John Wiley & Sons, New York,
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